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DETERMINATION OF THE ELECTRODE POTENTIAL OF CHROMIUM

By

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INTRODUCTION

The importance of an accurate knowledge of the potential developed between a metal and an aqueous solution of a salt of that metal becomes apparent at once when a study of the common cells is begun. From such study we come to realize that aside from the purely scientific or theoretical standpoint of the question there is a practical side as well.

In orderto assure the proper placing of the elements in the electromotive series an accurate determination of the electrode potentials is necessary. Many of these have already been accurately determined, some by direct and others by indirect methods; the latter based upon assumptions that may or may not be valid.

.Among those metals that have not been accurately determined is chromium. It was therefore suggested to the author that such a determination would prove of value, as mentioned above, both from a pure science and practical viewpoint. With these things in mind the author set out to make such a determination, if it were possible.

In order that sufficient experience to handle the admittedly more complex problem of determining the potential of chromium be obtained, it was decided to check up certain values as obtained by recent workers upon zinc.

The results thus obtained were not just what it was hoped they might be although the apparatus as used by Mr. David Schlesinger and the author did not have some of the refinements that the other workers had. That is, to say, this apparatus lacked for one thing a thermostatic control of temperature. This was in a certain measure unfair to the previous work that had been done, but it was desired

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to obtain some data that might be used in the solution of a problem connected with a laboratory course in which the refinements of thermostatic control could not be used to advantage. After the suggestion in regard to the use of finely divided zinc prepared electrolytically had been carried out, the attention of the author was again turned toward the real problem, that is the determination of the specific electrode potential of chromium.

THEORETICAL

The question of the source of the electromotive force of a cell arouses our interest in electro-chemical processes. A complete answer to this question involves a study of some of the simpler cells from the theoretical side. Those in which we shall be interested are those involving electro-chemical, rather than physical processes.

The common Daniell cell is familiar to most of us and is a good example of what we mean by a cell. Any such arrangement for performing electro-chemical reactions is know as a cell. While the general form of cells is the same, there are are two classes into which they may be divided, namely, electrolytic and voltaic. We find then in analyzing such a cell that it consists of, (a) a zinc electrode in a solution of zinc sulfate, (b) a copper electrode in a solution of copper sulfate from which the entire cell is formed by placing the two half cells in conducing contact. Such a combination will yield a current under suitable conditions, that is, by joining the terminals of the electrodes by a conductor.

When a change in state can be made to take place in some such manner as above in which reduction takes place at one electrode and oxidation at the other, it can be made to yield electrical energy. Reduction processes are connected with the giving up of electricity and oxidation processes with the taking on of charges. Whenever these two actions can be separated but yet be in electrical contact with one another, we have a cell.

The quantity of work that the system is capable of giving depends upon the initial and final states of the system. This then, involves the temperature, the concentration, the pressures, and the chemical reactions taking place. It is to be noted then that the driving

force or tendency toward chemical reaction in a cell is measured by the voltage or electromotive force that is developed. The work done per unit quantity of electricity flowing through the cell may be given as a definition of this quantity.

This then, shows how closely related are the transformations of energy accompanying a chemical reaction and the electromotive force it is capable of producing, if carried out in a cell, and that this force may be regarded as a measure to a certain extent of the energy change.

The electromotive force of a cell is made up of the sum of the forces produced at the junctions of dissimilar substances. Thus the electromotive forceof the Daniell cell is the algebraic sum of the force from the zinc to the zinc sulfate, that from the zinc sulfate solution to the copper sulfate solution, and that from the copper sulfate solution to the copper. The electromotive force produced at the junction of the two solutions is known as the liquid potential and that produced at the electrodes as the electrode potential.

While certain attempts at determination of absolute values of electrode potentials have been made, such as by the use of the dropping electrode method and the capillary electrometer, these have not been very successful. That is, to say, the values so far obtained are not as good as the comparative values that are always meant unless otherwise specified. Measurements made by the use of ordinary half cells as a basis of reference are more easily made, and from such measurements our data relative to the electrode potentials have been compiled. There are several standard reference electrodes in use and several scales are employed but we shall make use of the normal hydrogen electrode in all our considerations in which the potential

developed between a platinum electrode saturated with hydrogen gas under a pressure of one atmosphere dipping into a solution containing hydrogen ion at a concentration of one formula weight per liter is placed equal to zero.

From a consideration of the change in state which a cell undergoes there is developed the expression for the free energy decrease experienced in the process:-

$$-\Delta F = NRT \ln \frac{C_1}{C_2}$$

in which c_1 and c_2 are the initial and final concentrations, R is the gas constant, and T is the absolute temperature, while the log term is to the base e. With the aid of the other expression for the free energy decrease:-

$$-\Delta F = ENF$$

we are able to arrive at an expression whereby the change in the electromotive force developed by a given change can be calculated:-

$$E = \frac{NRT}{nF} \ln \frac{c_1}{c_2}$$

Making use of this relation for the change in free energy upon dilution, assuming that the solution is completely ionized and follows precisely the gas laws, Nernst arrived at the well known and important formula which goes by his name namely:-

$$E = E_0 + 2.3026 \times \frac{RT}{nF} \log_{10} \frac{C}{C_0}$$

where E is the potential difference for the ionic concentration C; E_0 is the electrode potential in the case where C_0 has the value unity; R is the gas constant with a value of 8.32 joules per degree; n is the valence of the ion; F is the farady or 96,000 coulombs. This gives then a method of determining the electrode potential E_0, if we know the other members of the equation.

Due to the very nature of some of the elements it is quite easily

seen that the use of a simple aqueous solution of a salt of the element whose electrode potential is to be measured combined with an electrode of this material is out of the question. Some of the metals exhibit such properties as passivity that quite materially affect an accurate determination of potentials by such a method. There have been as a result of these difficulties some very ingenious devices and methods brought forth for getting around them. It may be well at this time to pay some attention to a few of these that we may have before us the possibilities in the way of methods that have been tried.

Aluminum, as is well known, exhibits the tendency toward passivity. In attempting to get a value for the electrode potential of this metal Kahlenburg[2] found that the effect of a solution of sodium hydroxide was the same as amalgamation of the electrode. That is, to say, that in so far as the caustic solution acts as a solvent for the oxide of the metal and thereby removes the tendency toward passivity the mercury is thought to do likewise. The use of amalgams we find has been fairly general even in the work with non-aqueous solutions.

The potential developed by lithium was determined by Noyes and Keyes[3] by the use of the systems Li/LiCl + propylamine/Li-Hg(0.035 %) and Li-Hg LiOH/LiCl/KCl/nKCl nHgCl. In using such a dilute amalgam the action of the water upon the lithium was practically nil while in the propylamine there was no action. Then upon the assumption that the difference in potential betweenthe lithium and the lithium amalgam in propylamine is the same as would be given by the two in an aqueous solution they were able to get a value for the electrode potential of lithium. Similar methods have been used for other very reactive metals.

It is interesting to note that the potential of zinc, copper,

and silver have been determined by electrostatic measurements.[4] In this method a glass flask was covered with a layer of the metal and then a known charge applied. By means of an electrometer the values were determined for solutions of fairly high concentration, that is, normal and half normal.

Working upon the assumption, based upon theoretical considerations, that the difference between the electrode potential of a metal in ethyl alcohol and water for all metals has the same value, Roderburg and later other workers as A.Fisher[5] and V.B.Marquis[6] determined the potential of metals that have properties that render them difficult to handle in water solutions. This method has been applied to tungsten, uranium, and arsenic in particular and while the results that have been obtained may not be the best that might be desired, they are the best that have been brought forward so far.

These then, were the possibilities in the way of methods that had been tried that were open to the author. A study of the chemical behavior of chromium had to preceed any attempt at a determination of the potential as well as a general survey of the literature of the previous work upon the element in this connection.

It has been found that chromium can dissolve electrolytically in any one of three states, CrO, Cr_2O_3, CrO_3 according to the nature of the electrolyte and its temperature. The inactive state of the metal corresponds, perhaps, with the passive state of iron. The attainment of this passive state is not to be attributed to the presence on the metal of a thin layer of oxide, the hypothesis which is plausible for iron. It appears rather to imply that the surface, at least, of the metal differs in molecular arrangement according to the conditions and surroundings to which it is exposed: in short that

chromium appears to be an allotropic element. Chromium exists in three different states which are known as active, passive and intermediate. In each of these it shows a different chemical affinity and has a different chemical behavior.

The selection of proper working conditions necessitated then, as mentioned above, an historical treatment of the element.

HISTORICAL

Hittorf[7] found in investigating the electrochemical behavior of chromium that in dilute halogen acids or sulfuric acid, chromium dissolves on the application of heat with the formation of chromous compounds. Nitric, chloric, chromic, phosphoric, citric, tartaric, formic, and acetic acids, caustic potash and soda have, however, no action either hot or cold. In its electrical properties it is found to be electronegative, not only to zinc, but also to cadmium, iron, nickel, copper, mercury, and silver, and is inactive in solutions of these metals except in that it reduces mercuric or cupric to mercurous or cuprous salts. When employed as anode in solutions in which it is indifferent, it was found to become covered with a yellow film of chromic acid, and the loss of weight of the anode was found to correspond with the production of sexavalent chromium ions; this occurs even in solutions of hydrogen chloride in which chromium ordinarily dissolves with the formation of chromous salts. This he supposes to be due either to the decomposition of the water by the anion and subsequent formation of chromic acid from the liberated oxygen, or to the formation of a compound of sexavalent chromium with the anion and the decomposition of this compound by water; no such compound however is known to exist. In solutions of potassium thiocyanate or of an iodide, the chromium anode experiences no loss. A chain of the type Cr/KCl/NaNO /AgNO /Ag gave no electromotive force at 5°, and the same result was obtained when a dilute acid was substituted for the KCl solution. When the acid employed, however, was sufficiently strong to cause the chromium to dissolve and the evolution of hydrogen, an electro motive force of 1.056 volts was obtained. When the metal was used for the electrol-

ysis of melted KCl or ZnCl , totally different results were obtained, and the loss of weight of the anode proved bivalent chromium ions were produced, and similar results were found in solutions at 100° of the halogen acids,of potassium chloride,ammonium chloride,and in solutions of zinc and magnesium chlorides at higher temperatures.

In considering the inactivity of chromium he does notthink the theory of the oxide film as applied to iron applies to the case of chromium. In a second paper[8] he suggests this idea. Owing to the existence of the different classes of chromium compounds the metal may exhibit any potential between the two extreme values;the highest value corresponds with the active state in which chromium gives rise to the lower compounds. This active state is assumed when the metal is placed in sulfuric,oxalic,hydrofluosilicic, or the halogen acids at temperatures which are lower the more concentrated the acid; it is also active in fused halogen salts or their boiling solutions.

The metal becomes inactive when immersed in solutions containing free chlorine or bromine,or in strong oxidizing agents. The limiting values, however, last but a short time after removal from the liquids, the metal speedily assuming an intermediate state; the most stable active state is that produced by fused halogen salt. The activity is also lowered when the metal serves as an anode for a current produced either externally or internally, and with sufficiently strong currents chromic acid is produced, either by decomposition of water by anion and subsequent union of the metal and oxygen, or by the intermediate formation of a compound of the anion and chromium. When the metal is used as a cathode it rapidly assumes the active state.

A.Fisher[9] in undertaking the study of the electrochemistry of

the chromium group or sixth group metals says that the problem is complex because of three main reasons. These are: (1) The difficulty in preparing aqueous solutions of definite metal content; (2) The tendency to show passivity; (3) The preparation of absolutely pure metal of uniform size and shape. Fisher's paper treats only tungsten and uranium. He used the method used by Roderburg making use the relation

$$E.P._{(water)} - E.P._{(alcohol)} = Constant.$$

He found that solutions of WCl_6 in ethyl alcohol showed the least passivity and alcoholysis was minimized by suitable dilution and maintainance at low temperatures (2^o). The element W / W Cl_6 in ethyl alcohol and LiCl was prepared and compared with Cu / $CuCl_2$ in ethyl alcohol and LiCl which in turn was compared with Hg / $HgCl_2$ in ethyl alcohol and LiCl, referred to the standard calomel electrode on the absolute scale (-0.56 volt). $CuCl_2$ was selected because of its similarity to tungsten inregard to solubility and its nearness in the voltage series. By determining the conductivity in the alcohol solutions so as to arrive at the value of α, the electrode potential in alcohol gave the value for tungsten as 0.680. For copper, $E\,P_{(water)} - E\,P_{(alcohol)} = 0.071$ volt. From these values Fisher concludes that for tungsten, $E\,P_{(water)} = 0.680 - 0.071$ or 0.609 volts referred to $H_2 = 0$.

In undertaking the study of the electrode potential of chromium the literature on the electrolytic preparation of the pure metal was also reviewed.

By using a solution of 100 parts water to 25 parts $CrCl_3$ and working at a temperature of 88^o and a current density of 4.3 -5.3 amperes per square decimeter a good deposit of the metal was

obtained by Cowper and Coles[10]. It was found necessary, however, to to add an excess of hydrochloric acid to dissolve the precipitated oxide and form a clear solution. Solutions of the chromates require a high current density which is different for every concentration of the chromate and may in no case vary through very wide limits. The electrolysis of chromous chlorid shows a side reaction due to chlorine. Chromous sulfate is claimed to give very good deposits of the metal. The sulfate can be prepared by treating potassium dichromate with hydrochloric acid; the chromic chlorid obtained being rapidly reduced to chromous chloride by nascent hydrogen. This when treated with sodium acetate gave chromous acetate $Cr(Ac\,O)_2$, which when added in excess to dilute sulfuric acid constituted the electrolye. Air must be excluded from contact with the reacting substances however.

EXPERIMENTAL

In the laboratory of electrochemistry at Illinois zinc that has recently been amalgamated has been used in experiments on the electrode potentials of metals. The results obtained have varied so much that there was the desire to improve upon the method. Finely divided zinc as suggested by Horsch[11] was then tried. The metal was produced by rapid electrolysis of the zinc chloride solution in which a rod of pure zinc served as an anode and a platinum wire in the form of a spiral as the cathode. The current density was not kept absolutely constant, that is, it varied somewhat with successive preparations. According to Horsch this has no apparent effect except in the ease of washing the metal. The spongy metal so obtained was kept covered with a solution of zinc chloride at the concentration in which the E.M.F. was to be measured. Upon standing for some time a small amount of the zinc reacted with the water to form the hydroxide. This hydrolysis did not effect the utility of the zinc for after washing with dilute hydrochloric acid and then with water, the metal could be used as before.

The zinc chloride solution was prepared by dissolving C.P. zinc chloride in pure water. Hydrolysis occured to some extent and the hydroxide was removed by filtration. The normality of the solution was determined by Volhard's method for chlorides.

The Ag-AgCl electrode was prepared by first plating a platinum gauze with silver from a cyanide of silver solution and then the silver chloride formed as a black deposit by using the silver as an anode in a dilute solution of sodium chloride to which a small amount of HCl had been added. This electrode was standardized against hydrogen in 0.01 normal HCl and found to have a voltage of 0.4653

volts, this reading being the average value obtained from a number.

The complete cell was then set up as shown on the following page. It consisted of the chain Zn/$ZnCl_2$/ AgCl/Ag . A table of E.M.F. readings is given below and represents six cells as numbered.

(1)	(2)	(3)	Cell Number	(4)	(5)	(6)
1.1628	1.1580	1.1600		1.1605	1.1649	1.1580
1.1629	1.1550	1.1610		1.1604	1.1647	1.1572
1.1620	1.1850	1.1610		1.1607	1.1652	1.1582

These results show, in a measure, the very thing that it was desired to correct in the method as used in the class work. While only the values for 0.01 molal solution are given, the author is of the opinion that the data are enough to prove the uselessness of trying to use this as a class experiment in this form.

* * *

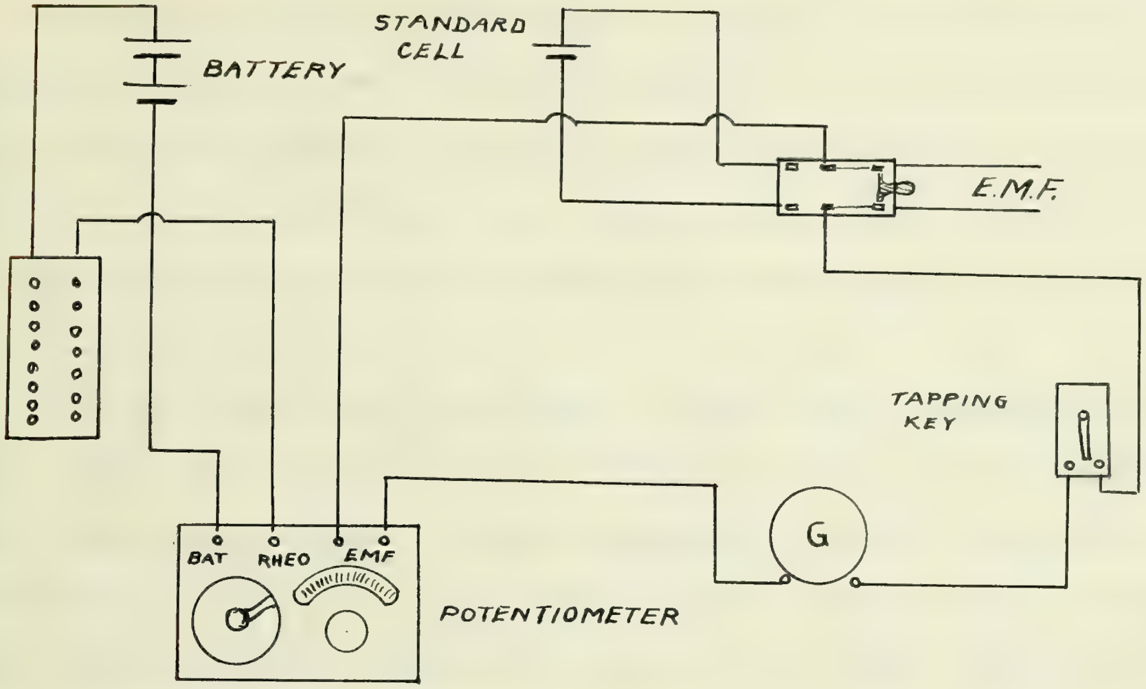
Experimental (Con't)

Work Done Upon Chromium in the Laboratory.

It was hoped that in a manner similar to that used by A.Fisher[12] a salt of chromium might be prepared which would be soluble in ethyl alcohol and then by means of the constant E.M.F. existing between the value for alcohol and water the electrode potential of the element arrived at. With this idea in mind the author prepared some anhydrous chromic chloride.

Metallic chromium was placed in a pyrex tube about three feet long and by passing dry chlorine over the red hot metal for some time a product was obtained. The chlorine was generated by dropping concentrated hydrochloric acid upon crystals of potassium permanganate. The gas was washed by passing through two bottles of water and then a third bottle of sulfuric acid which served to remove the water. A U-tube containing calcium chloride was also placed in the chain for the same purpose. The metal glowed strong-

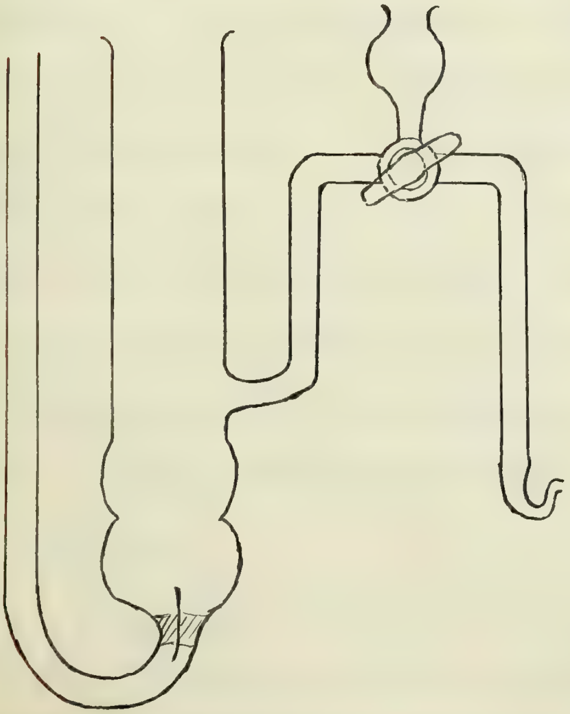
Set up as used in determining electrode potentials.

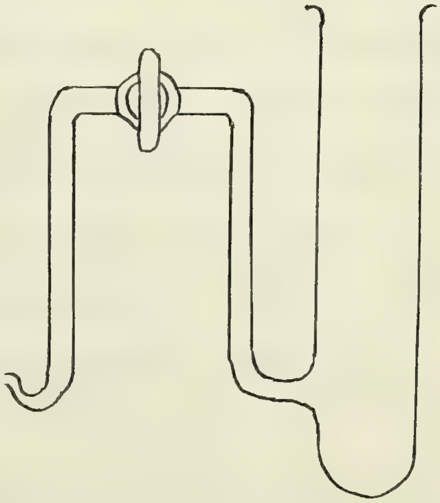


Calomel Half-cell

Sketches ← of →

Half-cell for metals.





ly after the reaction had begun showing that it was endothermic.

After cooling, the contents of the tube were removed and found to consist of a mixture of products. A fine apple blossom colored powder that had sublimed away from the rest of the mass and a large bulk of purple crystals containing some of the metal intermixed with them, were obtained. From discriptions found in the literature it was decided that both the crystalline mass and the fine powder were chromic chloride.

It was found that the chromic chloride was insoluble in alcohol and hence this line of endeavor reached an end. A more soluble salt was sought after. There appeared to be no chromic salt that was easily prepared with the means at hand suitable for the purpose. In the literature a method for preparing chromous chloride from the chromic salt is discribed.

The purple crystals discribed above were placed in a pyrex tube and it was hoped that by passing hydrogen over them in a heated condition they would be reduced to the easily soluble chromous chloride. The hydrogen was obtained from a cylinder of electrolytic hydrogen. Even strongly heating the chromic chloride with the gas did not give a quantity of the chromous salt worth separating. There was some to be sure, but it was intermingled so thoroughly with the dark mass of residue that it was impossible to obtain even a sample of the salt without hoping to be able to work with it. A repetition of the operation using a fused quartz tube in order that higher temperatures might be reached, yielded the same kin d of results.

A chromium electrode was prepared by electrolyzing a solution of chromic chloride with a current density of about four amperes

per square centimeter. The chromium was plated upon a piece of platinum foil but was not very adherent. That is, due to some defect in the current density or the temperature the deposit was crystalline instead of the smooth coating that it had been hoped would be obtained. This defect, it is thought, could have been corrected had there been any real need for the metal. Since a suitable electrolyte in which to make the determination had not been found the metal could not have been used as an electrode even, if it had have been obtained in the form of an even smooth coating.

A SUMMARY OF THE EXPERIMENTAL RESULTS OBTAINED.

Finely divided zinc was prepared by the electrolytic deposition of the metal upon a platinum wire from a solution of the chloride.

Using the chain $Zn/ZnCl_2/AgCl/Ag$ results were obtained which did not seem to warrant the use of the experiment as a class experiment.

It was found that the method of Roderburg wherein the difference of E.P. between absolute alcohol and water is made use of,was not applicable in the case of chromic chloride since it is not soluble in alcohol.

An attempt to make anhydrous chromous chloride was a failure.

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